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(54) **Fluorolefin copolymer, process for production thereof and composition containing said copolymer.**

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US-A-2 836 582
US-A-3 240 757

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Description

This invention relates to a fluoroolefin copolymer, a process for production thereof, and a composition containing the copolymer. More specifically, this invention relates to a fluoroolefin copolymer composed substantially of a fluoroolefin, a carboxylic acid vinyl ester and a vinyl ether, and to a process for producing the copolymer in high yields by utilizing the copolymerizability of the individual monomers.

Fluoroolefin polymers have found extensive use for their useful properties such as chemicals resistance, heat resistance, abrasion resistance and non-tackiness. Because of their high melting points, they have the defect of requiring melting and baking at high temperatures in film formation. Furthermore, since they are insoluble in solvents, they can be used only in the form of an emulsion or dispersion and cannot be formulated into paints having good storage stability. In order to remedy these defects, attempts have been made heretofore to copolymerize the fluoroolefin with vinyl monomers. For example, Japanese Laid-Open Patent Publications No. 11915/1974 proposes a solvent-soluble coating composition comprising vinylidene chloride, hexafluoropropylene (HFP for short) and vinyl acetate. US—A— 4 151 340 proposes a solvent-soluble polymer composed of a fluoroolefin and cyclohexyl vinyl ether and having high rigidity. Cyclohexyl vinyl ether is a special monomer which is not commercially available in general and is expensive. US—A—2 834 767 proposes a copolymer of a fluoroolefin with a vinyl ether which, however, gives only a short film.

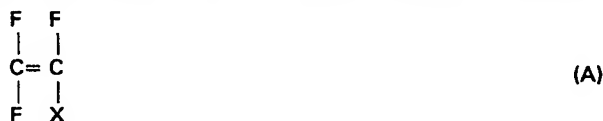
US—A—3 240 757 describes copolymers of 3,3,3-trifluoro-2-trifluoromethyl propene and certain ethylenically unsaturated monomers copolymerizable therewith, particularly fluorine-containing elastomeric and resinous polymeric compositions.

It is the object of this invention to provide fluoroolefin polymers free from the foregoing defects.

The present inventors extensively worked for achieving this object, and found that a copolymer obtained by copolymerizing specific proportions of a fluoroolefin, a carboxylic acid vinyl ester, an alkyl-containing vinyl ether and a optionally hydroxyl-containing vinyl ether is inexpensive and has high rigidity and solubility in solvents.

Thus, according to this invention, there is provided a fluoroolefin copolymer having an inherent viscosity of from 0.05 to 2.0 dl/g and composed of

(I) 10 to 70 mole% of monomeric units derived from a fluoroolefin represented by the general formula



wherein X is H, Cl F, CF₃, OCF₃ or OC₃F₇,

(II) 5 to 60% of monomeric units derived from a vinyl carboxylate represented by the general formula



wherein R₁ represents an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 17 carbon atoms, (III) 5 to 70 mole% of monomeric units derived from a vinyl ether having an alkyl group with 1 to 8 carbon atoms, and

(IV) 0 to 30 mole% of monomeric units derived from a hydroxyl-containing vinyl ether represented by the general formula



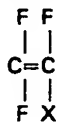
wherein R₂ represents an alkylene group having 1 to 6 carbon atoms.

According to this invention, there is also provided a process for producing the aforesaid fluoroolefin copolymer, which comprises polymerizing the aforesaid component monomers in the presence of a radical initiator at a temperature of from -20°C to 130°C.

The invention further provides a composition comprising a fluoroolefin copolymer having an inherent viscosity of 0.05 to 2.0 dl/g and composed of

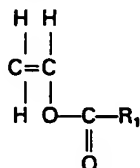
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(I) 10 to 70 mole% of monomeric units derived from a fluoroolefin represented by the general formula



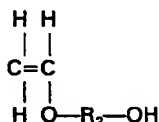
wherein X is H, Cl, F, CF₃, OCF₃ or OC₃F₇,

(II) 5 to 60% of monomeric units derived from a vinyl carboxylate represented by the general formula



wherein R₁ represents an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 17 carbon atoms,
(III) 5 to 70 mole% of monomeric units derived from a vinyl ether having an alkyl group with 1 to 8 carbon atoms, and

(IV) 0 to less than 5 mole% of monomeric units derived from a hydroxyl-containing vinyl ether represented by the general formula



wherein R₂ represents an alkylene group having 1 to 6 carbon atoms;
and an organic solvent.

Examples of the fluoroolefin of general formula (A) which is a source of the monomeric units (I) in the copolymer of this invention, are tetrafluoroethylene, chlorotrifluoroethylene and hexafluoropropylene. The content of the monomeric units (I) in the copolymer is 10 to 70 mole% preferably 20 to 60 mole%. If the content is less than 10 mole% the characteristics of the fluoroolefin is not exhibited in the copolymer. If it exceeds 70 mole%, the adhesion of the copolymer to a substrate is poor.

Examples of the vinyl carboxylate of general formula (B) which is a source of the monomeric units (II) include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl caproate, vinyl Versatate® (a vinyl ester of C₉—C₁₀ carboxylic acids), vinyl laurate, vinyl stearate, vinyl benzoate, vinyl p-t-butylbenzoate and vinyl salicylate. Vinyl Versatate® and vinyl benzoate are especially preferred because the use of these in small amounts can lead to an increase in the hardness of a coated film from the copolymer. The content of the monomeric units (II) in the copolymer is 5 to 60 mole%, preferably 10 to 50 mole%. If it is less than 5 mole%, a coated film prepared from the copolymer has low rigidity and low hardness and remarkably gathers dust. If it exceeds 60 mole%, the copolymer forms a brittle coated film.

Examples of the vinyl ether having a C₁—C₈ alkyl group are methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, t-butyl vinyl ether, n-pentyl vinyl ether, n-hexyl vinyl ether, n-octyl vinyl ether, and 2-ethylhexyl vinyl ether. The content of the monomeric units (III) in the copolymer is 5 to 70 moles%, preferably 10 to 60 mole%. If it is less than 5 mole%, the resulting copolymer is undesirably in a low yield. If it exceeds 70 mole%, the copolymer has a decreased fluorine content and its characteristics as a fluorine polymer are degraded.

Examples of the hydroxyl-containing vinyl ether of general formula (C) which is a source of the monomeric units (IV) are hydroxymethyl vinyl ether, hydroxyethyl vinyl ether, 3-hydroxypropyl vinyl ether, 2-hydroxypropyl vinyl ether, 4-hydroxybutyl vinyl ether, 3-hydroxybutyl vinyl ether, 2-hydroxy-2-methylpropyl vinyl ether, 5-hydroxypentyl vinyl ether and 6-hydroxyhexyl vinyl ether. The content of the monomeric units (IV) in the copolymer is 0 to 30 mole%, preferably 5 to 30 mole%, more preferably 7 to 20 mole%. If it is less than 5 mole%, the curability of the copolymer with the curing agent is insufficient. If it exceeds 30 mole%, the copolymer has a reduced solubility in solvents, and a paint prepared by mixing the copolymer with a solvent and a curing agent has so sort a gelation time that its applicability decreases.

The copolymer of this invention may contain other monomeric units derived from other copolymerizable vinyl monomers so long as the inclusion of the other units does not impair the intended effects of the invention. Examples of such other vinyl monomer include olefins such as ethylene, propylene and butene-1; vinyl halides such as vinyl chloride, vinylidene chloride, vinyl fluoride and vinylidene fluoride; acrylic acid esters having alkyl of 1 to 8 carbon atoms; methacrylic acid esters having alkyl of 1 to 8

carbon atoms. The suitable content of the other vinyl monomer units is less than 30 mole%.

The copolymer of this invention has an inherent viscosity, determined in tetrahydrofuran at 25°C, of 0.05 to 2.0 dl/g, preferably 0.2 to 1.0 dl/g. If the inherent viscosity is less than 0.05 dl/g, the copolymer has low mechanical strength. If it exceeds 2.0 dl/g, a solution of the copolymer has an excessively high viscosity so that the application of a coating prepared from it becomes difficult. When the copolymer of this invention contains a hydroxyl group, it preferably has a hydroxyl value of 20 to 200 mg KOH/g, especially 30 to 120 mg KOH/g. If its hydroxyl value is less than 20 mg KOH/g, the copolymer has a long curing time in the presence of a curing agent, and the mechanical strength of a film from the copolymer does not increase to a high level. On the other hand, if its hydroxyl value exceeds 200 mg KOH/g, the curing time is excessively short, and therefore the applicability of a composition obtained from it is poor. Moreover, a cured product of the copolymer is brittle.

The copolymer of this invention can be produced by mixing 10 to 70 mole% of the fluoroolefin of general formula (A), 5 to 60% of the vinyl carboxylate of general formula (B), 5 to 70 mole% of the alkyl-containing vinyl ether and up to 30 mole% of the hydroxyl-containing vinyl ether of general formula (C), and polymerizing the mixture in the presence of a radical initiator by a batch-wise, semi-continuous or continuous operation in accordance with a known technique such as bulk polymerization, solution polymerization, suspension polymerization or emulsion polymerization.

The radical initiator used in this invention has a moderate decomposition speed at the copolymerization reaction temperature. Examples include diacyl peroxides such as acetyl peroxide and benzoyl peroxide; ketone peroxides such as methyl ethyl ketone peroxide and cyclohexanone peroxide; hydroperoxides such as hydrogen peroxide, t-butyl hydroperoxide and cumene hydroperoxide; dialkyl peroxides such as di-t-butyl peroxide and dicumyl peroxide; alkyl peroxyesters such as t-butyl peroxyacetate and t-butyl peroxyvalerate; azo compounds such as azobisisobutyronitrile; and persulfates such as ammonium persulfate and potassium persulfate. As required, an inorganic reducing agent such as sodium hydrogen sulfite and sodium pyrosulfite, or an organic reducing agent such as cobalt naphthenate and dimethylaniline may be used in the copolymerization. The suitable amount of the radical initiator is 0.01 to 10% by weight based on the total weight of the monomers, and the suitable weight of the reducing agent is 0.01 to 5% by weight on the same basis.

The copolymerization is carried out usually at a temperature of from -20°C to 130°C and a pressure of 0.98 to 98.1 bar (1 to 100 kg/cm²), preferably 4.9 to 58.9 bar (5 to 60 kg/cm²).

An aromatic hydrocarbon such as toluene, xylene and ethylbenzene, a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone, an acetic acid ester such as ethyl acetate, propyl acetate, butyl acetate and isobutyl acetate, and an alcohol such as isopropanol, n-butanol and ethyl Cellosolve® may be added to the copolymer of this invention. The mixing ratio of the copolymer to the solvent is suitably from 95:5 to 5:95, preferably from 90:10 to 10:90, by weight.

Furthermore, a curing agent may be added to the copolymer of this invention.

Where the copolymer of this invention contains the hydroxyl-containing vinyl ether units, the hydroxyl groups therein constitute crosslinking sites. Hence, by incorporating a curing agent capable of reacting with the hydroxyl groups, the copolymer can be cured at room temperature or at 50 to 300°C, preferably 60 to 250°C. Typical examples of the curing agent are aminoplasts, polyisocyanate compounds, blocked polyisocyanate compounds, polybasic acids and polybasic acid anhydrides.

Typical examples of the aminoplasts are condensates formed between amino group-containing compounds such as melamine, urea, acetoguanamine or benzoguanamine and aldehyde compounds such as formaldehyde, paraformaldehyde, acetaldehyde or glyoxal by known conventional methods, and products obtained by etherifying these condensates with alcohols. Those partially or completely etherified with C₁-C₄ alcohols are preferred. Specific examples of the aminoplasts include hexamethyl etherified methylolmelamine, hexabutyl etherified methylolmelamine, methyl-butyl mixed etherified methylolmelamine, methyl etherified methylolmelamine, butyl etherified methylolmelamine and isobutyl etherified methylolmelamine. Particularly, from the viewpoint of the compatibility with the copolymer of this invention, the use of methyl etherified methylolmelamine is desirable.

Typical examples of the polyisocyanate compounds include aliphatic diisocyanates such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate and tetramethylene diisocyanate; alicyclic diisocyanates such as xylylene diisocyanate, methylcyclohexane-2,4-(or 2,6)-diisocyanate, isophorone diisocyanate and 4,4'-methylene-bis(cyclohexylisocyanate); adducts of the aforesaid diisocyanates with polyhydric alcohols or carbon dioxide gas; polyisocyanate containing a biuret linkage obtained by reacting the aforesaid diisocyanates with water; and polyisocyanates having an isocyanurate ring obtained by polymerizing the aforesaid diisocyanates.

Examples of the blocked polyisocyanates may be those obtained by blocking the aforesaid polyisocyanate compounds with known conventional blocking agents typified by alcohols, compounds having phenolic hydroxyl groups, oximes, acetoacetic acid esters and N-monosubstituted carboxylic acid amides.

Typical examples of the polybasic acids are acrylic resins having at least 2 carboxyl groups per molecule; polyester resins having at least 2 carboxyl groups per molecule, and aromatic polybasic acids such as trimellitic acid and pyromellitic acid.

Typical examples of the polybasic acid anhydrides are succinic anhydride, trimellitic anhydride, pyromellitic anhydride, and vinyl polymers having a carboxylic acid anhydride group.

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As required, the above composition may include pigments, resins, solvents, leveling agents, antiflooding agents, antioxidants, ultraviolet absorbers, etc.

The copolymer of this invention is soluble in organic solvents, and an organic solvent solution of the copolymer forms a film having excellent weatherability, water repellency, non-tackiness, soiling resistance and chemical resistance upon evaporation of the solvent at room temperature.

In particular, the copolymer of this invention, which has hydroxyl groups forms a film having better properties when it is cured with a curing agent.

The copolymer of this invention shows excellent utility in surface coating agents for steel materials, wooden products, ceramic products, glass products and plastic products, water-repellent and oil-repellent agents for textile finishing, non-tacky coating agents, sliding bearings, a sheath material for optical fibers, solar collectors and physical or chemical materials for medical therapy. The copolymer of this invention is also useful as baking paints for metals, paints for external finishing of buildings, paints for roofs of buildings in districts where snowfall is heavy, ship paints, automobile paints, and aircraft paints.

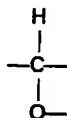
The following examples illustrate the present invention more specifically.

Examples 1—7 and Comparative Example 1

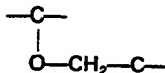
In each run, a 100 ml stainless steel pressure tube was charged with 50 cc of methyl isobutyl ketone, 0.5 g of tert.-butyl peroxyvalate (TBP for short), ethyl vinyl ether (EVE for short) in the amount indicated in Table 1, and the vinyl carboxylate having a C₈ alkyl group (Veova-9, a tradename for a product of Shell Chemical Co.) or vinyl benzoate (BzVE for short) in the amount indicated in Table 1. Then, the reaction tube was cooled to -70°C by dry ice-methanol. Nitrogen gas was blown into the tube to remove air. Then, a predetermined amount of liquefied hexafluoropropylene (HFP for short) or chlorotrifluoroethylene (CTFE for short) was introduced into the tube, and the tube was sealed up.

The reaction tube was put in a water bath heated at 60°C, and the mixture was reacted for 16 hours under shaking. The reaction mixture in the tube was precipitated from 10 times its amount of methanol. The precipitate was dried for one day at 80°C, and its yield was measured. The polymer was dissolved in 100 cc of acetone, and purified by precipitating it from 1 liter of methanol, followed by drying. The fluorine content, NMR, inherent viscosity and glass transition temperature of the product were measured.

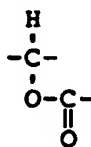
As a result of its NMR measurement (by Model JNM—MH60 supplied by Nippon Electronics Co., Ltd.; internal standard, tetramethylsilane), the proton of



assigned to ethyl vinyl ether appeared at 3.9—4.6 ppm, and the protons of



appeared at 3.2—3.9 ppm. The proton of



assigned to Veova-9 also appeared at 4.6—5.9 ppm.

Ethyl vinyl ether/Veova-9 (mole ratio)=

$$\frac{\text{Peak area of } (3.2-3.9) + (3.9-4.6)}{3} \bigg/ \frac{\text{Peak area of } (4.6-5.9)}{1}$$

The fluorine content was measured by fluorine colorimetry in accordance with the alizarin complexone method.

The inherent viscosity was determined by an Ubbelohde's viscometer for a 1% tetrahydrofuran solution of the polymer at 25°C.

The glass transition point was measured by TGA—DSC.

Table 1

		Example							Comp. Example
		1	2	3	4	5	6	7	
Monomers charged [g(mole%)]	HFP	13.5(30)	14.0(35)	18.5(41)	-	13.5(30)	22.5(50)	15.6(30)	30.0(50)
	CTFE	-	-	-	11.8(35)	-	-	-	-
	EVE	10.8(50)	6.7(35)	11.2(52)	8.4(40)	10.8(50)	6.5(30)	15.1(60)	14.4(50)
	Veova-9	11.9(20)	15.8(30)	4.2(7)	14.4(25)	-	11.9(20)	6.9(10)	-
	BzVE	-	-	-	-	8.9(20)	-	-	-
Amount of the polymer (g)		34.0	33.2	31.9	31.8	31.2	31.9	30.5	41.6
Yield of the polymer (%)		95.6	91.0	94.1	91.9	94.0	78.0	81.1	93.7
Composition of the polymer (mole%)	HFP	27	32	43	-	28	40	38	48
	CTFE	-	-	-	33	-	-	-	-
	EVE	52	35	50	39	51	36	50	52
	Veova-9	21	33	7	28	-	24	12	-
	BzVE	-	-	-	-	21	-	-	-
Conversions to the polymer (%) (*1)	HFP	85.3	82.2	97.3	-	88.4	64.0	94.2	91.3
	CTFE	-	-	-	84.9	-	-	-	-
	VE	98.5	90.2	89.7	87.2	96.6	95.4	61.6	98.6
	Veova-9	99.4	99.1	92.1	99.1	-	95.0	94.2	-
	BzVE	-	-	-	-	98.9	-	-	-
Inherent viscosity (dL/g)		0.23	0.17	0.29	0.25	0.26	0.13	0.19	0.24
Glass transition temp.(oC)		12	17	8	19	27	23	10	-2

Note to Table 1.

(*1): That portion of the charged monomers which was converted to the polymer.

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The above polymers were all soluble in organic solvents such as ethyl acetate, butyl acetate, acetone, methyl ethyl ketone, toluene, xylene and tetrahydrofuran.

Thirty grams of each of the polymers obtained in Examples 1, 3 and 5 and Comparative Example 1 was dissolved in a mixed solvent composed of 15 g of toluene and 15 g of methyl isobutyl ketone to obtain a colorless transparent solution. Ten grams of titanium dioxide <1> was added, and the mixture was ball-milled for 24 hours to prepare a white paint. The paint was coated by an applicator on a steel sheet (JIS G-3141) degreased with methyl ethyl ketone, and dried for 4 hours 110°C to form a coated film having a thickness of 30 to 40 μm . The properties of the coated film were measured, and are shown in Table 2.

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Table 2

		Example 1	Example 3	Example 5	Comparative Example 1
Hardness	Pencil	H	F	2H	2B
Adhesion	Crosscut	100/100	95/100	100/100	50/100
Chemical resistance	5% NaOH, 24 hrs., spot test	⊙	⊙	⊙	⊙
Water repellency	Repellency of water	⊙	⊙	⊙	⊙
Soiling resistance	Lipstick, washing with soap solution	⊙	⊙	⊙	⊙
Weatherability	Sunshine Weatherometer, 1500 hrs.	⊙	⊙	○	⊙
Tackiness	Coating of carbon black; washing with soap solution 24 hrs. later	⊙	○	⊙	x

Standards of evaluation

⊙ : No change (no adhesion)

○ : Very slight change (very slight adhesion)

x : Completely changed (adhered)

(The parenthesized standards apply to tackiness.)

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Example 8

A 2-liter electromagnetically stirred autoclave was charged with 525 g of methyl isobutyl ketone 92 g of Veova-9 and 231 g of isobutyl vinyl ether, and was purged with nitrogen under 9.8 bar (10 kg/cm²). This operation was repeated, and then 277 g of liquefied HFP under nitrogen pressure was charged into the autoclave.

The proportion of the monomer charged was 40 mole% of HFP, 50 mole% of isobutyl vinyl ether and 10 mole% of Veova-9.

The autoclave was then heated to 60°C, and a solution of 10 g of TBP in 76 g of methyl isobutyl ketone was added dropwise for 6 hours. After the addition, the temperature was raised to 70°C, and the mixture was maintained at this temperature for 2 hours. The pressure in the initial stage of the reaction was 6.7 bar (6.8 kg/cm²), but was 0.99 (1.0 kg/cm²) at the end of the reaction. The non-volatile content of the reaction mixture after the reaction was 47.9%. This means that the amount of the polymer formed was 575 g, and therefore, the yield of the polymer formed was 575 g, and therefore, the yield of the polymer based on the total weight of the monomers was 95.8%.

The resulting polymer was found to consist of 39 mole% of HFP, 51 mole% of isobutyl vinyl ether and 10 mole% of Veova-9 from the fluorine content and the NMR spectrum. The conversions of these monomers to the polymer were calculated as 93.9%, 97.4%, and 97.8%, respectively. The polymer had an inherent viscosity of 0.19 dl/g, and a glass transition temperature of 10°C.

Example 9

The same autoclave as used in Example 8 was charged with 525 g of methyl isobutyl ketone, and then purged twice with nitrogen under <1> 9.8 bar (10 kg/cm²). A 1-liter pressure vessel was cooled to -30°C with dry ice-methanol. From a tetrafluoroethylene (TFE for short) bomb, an excess of liquefied TFE was taken into the pressure vessel through a pipe. The pressure vessel was then heated to introduce 244 g of TFE into the autoclave. When the autoclave was heated to 60°C with stirring, the pressure reached 33.4 bar (34 kg/cm²). A mixture of 176 g of EVE and 180 g of BzVE was added dropwise from the monomer tank, and a mixture of 10 g of TBP and 75 g of methyl isobutyl ketone was added dropwise from a catalyst tank, uniformly over the course of 6 hours.

The proportion of the monomers charged was 40 mole% for TFE, 40 mole% for EVE and 20 mole% for BzVE.

With the progress of the polymerization, the pressure dropped, and reached 2.9 bar (3 kg/cm²) after the lapse of 10 hours. The non-volatile content of the reaction mixture after the reaction was 46.7%. This means that the amount of the polymer formed was 560 g, and its yield based on the entire monomers was 93.3%.

From the fluorine content and NMR spectrum as in Example 1, the resulting polymer was found to consist of 39 mole% of TFE, 41 mole% of EVE and 20 mole% of BzVE. The conversions of the individual monomers to the polymer were calculated as 92.2%, 96.6% and 94.4%, respectively. The polymer had an inherent viscosity of 0.15 dl/g, and a glass transition temperature of 22°C.

The properties of coated films prepared as in Example 1 from the polymers obtained in Examples 8 and 9 were measured, and are shown in Table 3 below.

Table 3

	Example 8	Example 9
Hardness	F	H
Adhesion	100/100	100/100
Chemical resistance	⊙	⊙
Water repellency	⊙	⊙
Soiling resistance	⊙	⊙
Weatherability	⊙	○
Tackiness	⊙	⊙

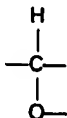
Examples 10—14

In each run, a 100 ml stainless steel pressure tube was charged with 50 cc of methyl isobutyl ketone (MIBK for short), 0.5 g of TBP, EVE in the amount indicated in Table 4, 4-hydroxybutyl vinyl ether (HBVE for short) in the amount indicated in Table 4, and Veova-9 (VV-9 for short) or BzVE in the amount indicated in Table 4, and cooled to -70°C on a dry ice-methanol bath. Nitrogen gas was blown into the pressure tube to

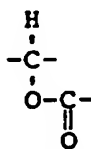
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remove oxygen from it. HFP, CTFE or TFE was introduced into the tube as in aforesaid examples, and the tube was sealed up. The sealed pressure tube was put in a water bath kept at 60°C, and the reaction was carried out for 16 hours under shaking. The reaction mixture in the tube was poured into 10 times its amount of methanol. The precipitate was dried at 80°C for 12 hours, and the yield of the resulting polymer was measured. The polymer was dissolved in 100 ml of acetone and then re-precipitated from 1 liter of methanol to purify it. The purified polymer was dried, and its fluorine content, NMR, inherent viscosity and glass transition temperature were measured as in Example 1.

The NMR measurement showed that protons of



assigned to the alkyl vinyl ether (b mole%) and the hydroxybutyl vinyl ether (c mole%) appeared at 3.9 to 4.6 ppm, and protons of



assigned to the vinyl carboxylate (d mole%) appeared at 4.6 to 5.9 ppm.

Hence, the mole ratio of

$$(b + c)/d = [\text{peak area of (3.9—4.6)}]/[\text{peak area of (4.6—5.9)}] \quad (1)$$

$$c + d = 100 - (a + b) \quad (2)$$

(a represents the mole% of HFP, CTFE or TFE).

From (1),

$$d = (b + c) \times \frac{[\text{peak area of 4.6—5.9}]}{[\text{peak area of (3.9—4.6)}]}$$

When d is substituted for d in equation (2), the following equation is given.

$$c + (b + c) \frac{[\text{peak area of 4.6—5.9}]}{[\text{peak area of (3.9—4.6)}]} = 100 - (a + b)$$

From the above equation, c (the mole% of hydroxybutyl vinyl ether) and d (the mole% of the vinyl carboxylate) can be obtained.

The hydroxyl values of the resulting copolymers were measured by the acetylation method using acetic anhydride, and the mole% of hydroxybutyl vinyl ether was calculated on the basis of the hydroxyl value.

The results are shown in Table 4.

Table 4

		Example				
		10	11	12	13	14
Monomers charged [g (mole%)]	HFP	18.1 (40.1)	12.9 (29.9)	20.1 (40.0)		
	CTFE				15.6 (40.0)	16.1 (40.1)
	TFE					8.7 (30.1)
	EVE	6.5 (30.0)	5.2 (25.1)	7.2 (29.8)	7.2 (29.9)	9.3 (19.9)
	HBVE	3.5 (10.0)	5.0 (15.0)	7.8 (20.1)	3.9 (10.0)	
	W-9	11.9 (19.9)	17.0 (30.0)		13.3 (20.1)	5.9 (9.9)
	BzVE			5.0 (10.1)		
Amount of the polymer (g)		36.7	37.3	38.0	36.9	36.2
Yield of the polymer (%)		91.8	93.5	94.8	92.2	90.5

Table 4 (continued)

		Example				
		10	11	12	13	14
Composition of the polymer (mole%)	HFP	37.7	30.0	39.8	40.7	41.1
	CTFE					29.1
	TFE					19.3
	EVE	31.5	25.0	30.2	30.7	
	HBVE	9.9	14.6	19.8	9.5	
	VV-9	20.9	30.4		19.1	
Conversions to the monomers (%)	BzVE			10.2		10.5
	HFP	86.7	93.0	94.5	94.9	92.5
	CTFE					87.4
	TFE					87.1
	EVE	96.9	92.3	95.8	95.8	
	HBVE	91.4	90.0	93.6	87.2	
Inherent viscosity (dl/g) Hydroxyl value (mg KOH/g) Glass transition temp. (°C) Fluorine content (wt.%)	VV-9	96.6	94.1	96.0	88.9	94.9
	BzVE					
	Inherent viscosity (dl/g)	0.27	0.22	0.31	0.26	0.19
	Hydroxyl value (mg KOH/g)	44.0	60.2	90.5	47.1	110.4
Glass transition temp. (°C)		14	25	24	15	21
	Fluorine content (wt.%)	32.5	24.4	38.0	19.6	31.2

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The above copolymers were all soluble in organic solvents such as ethyl acetate, butyl acetate, acetone, methyl ethyl ketone, tetrahydrofuran, carbon tetrachloride, toluene and xylene.

Examples 15—19

5 Copolymers having the compositions shown in Table 5 were obtained by the same polymerization and after-treatment as in Example 10.

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Table 5

	Example				
	15	16	17	18	19
HFP	14.7 (33.5)	13.2 (31.4)	16.3 (36.9)	15.0 (34.6)	12.2 (32.9)
n-propyl vinyl ether	5.3 (21.1)				
n-Butyl vinyl ether		6.5 (23.2)			
t-Butyl vinyl ether			8.3 (28.1)		
n-Hexyl vinyl ether				8.0 (21.7)	
2-Ethylhexyl vinyl ether					7.3 (18.9)
2-Hydroxyethyl vinyl ether	4.0 (15.4)				3.3 (15.6)
3-Hydroxypropyl vinyl ether		4.3 (15.2)	4.6 (12.0)		
5-Hydroxypentyl vinyl ether					
6-Hydroxyhexyl vinyl ether				7.1 (17.1)	
W-9	16.1 (30.0)	10.3 (20.0)			
Veova-10 (*)		5.7 (10.2)			
Vinyl pivalate			6.0 (15.9)	9.8 (26.6)	
Vinyl laurate			4.7 (7.1)		
Vinyl stearate					10.2 (13.5)
BzVE					7.0 (19.1)
Amount of the polymer (g)	36.8	36.5	36.9	36.9	36.2
Total polymer yield (%)	91.2	91.3	92.5	91.0	91.3

- to be continued -

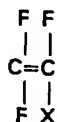
Table 5 (continued)

		Example				
		15	16	17	18	19
Composition of the polymer (mole%)	HFP	35.0	32.1	37.0	35.0	32.5
	n-Propyl vinyl ether	21.0				
	n-Butyl vinyl ether		23.0			
	t-Butyl vinyl ether			28.0		
	n-Hexyl vinyl ether				21.5	
	2-Ethylhexyl vinyl ether					18.7
	2-Hydroxyethyl vinyl ether	15.2				15.4
	3-Hydroxypropyl vinyl ether		15.0			
	5-Hydroxypentyl vinyl ether			12.1		
	6-Hydroxyhexyl vinyl ether				17.0	
	W-9	28.8	19.9			
	Veova-10 (*)		10.0			
	Vinyl pivalate			15.7	26.5	
	Vinyl laurate			7.2		
	Vinyl stearate					13.4
	BzVE					20.0
Inherent viscosity (dl/g)		0.26	0.20	0.21	0.23	0.19
Hydroxyl value (mg KOH/g)		62.3	57.2	48.8	66.6	53.1
Glass transition temperature (°C)		15	10	30	17	11
Fluorine content (wt.%)		29.1	24.9	30.3	27.9	22.8

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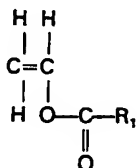
Claims

1. A fluoroolefin copolymer having an inherent viscosity of from 0.05 to 2.0 dl/g and composed of
 (I) 10 to 70 mole% of monomeric units derived from a fluoroolefin represented by the general formula



wherein X is H, Cl, F, CF₃, OCF₃ or OC₃F₇,

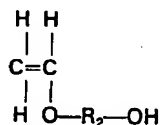
- (II) 5 to 60% of monomeric units derived from a vinyl carboxylate represented by the general formula



wherein R₁ represents an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 17 carbon atoms,

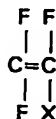
- (III) 5 to 70 mole% of monomeric units derived from a vinyl ether having an alkyl group with 1 to 8 carbon atoms, and

(IV) 0 to 30 mole% of monomeric units derived from a hydroxyl-containing vinyl ether represented by the general formula



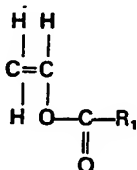
wherein R₂ represents an alkylene group having 1 to 6 carbon atoms.

2. The copolymer of claim 1 wherein the fluoroolefin is tetrafluoroethylene.
3. The copolymer of claim 1 wherein the fluoroolefin is chlorotrifluoroethylene.
4. The copolymer of claim 1 wherein the fluoroolefin is hexafluoropropylene.
5. The copolymer of claim 1 wherein the vinyl carboxylate is a vinyl ester of a carboxylic acid having 9 to 10 carbon atoms.
6. The copolymer of claim 1 wherein the vinyl carboxylate is vinyl benzoate.
7. The copolymer of claim 1 which contains 5 to 30 mole% of the monomeric units (IV), and has a hydroxyl value of 20 to 200 mg KOH/g.
8. A process for producing a fluoroolefin copolymer, which comprises polymerizing in the presence of a radical initiator and at a temperature of from -20°C to 130°C 10 to 70 mole% of a fluoroolefin represented by the general formula



wherein X is H, Cl, F, CF₃, OCF₃ or OC₃F₇,

- 5 to 60 mole% of a vinyl carboxylate represented by the general formula



wherein R₁ represents an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 17 carbon atoms,

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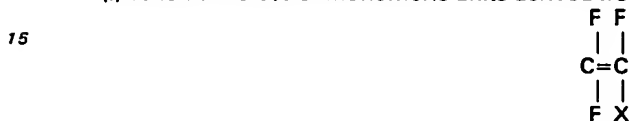
5 to 70 mole% of a vinyl ether having an alkyl group with 1 to 8 carbon atoms, and 0 to 30 mole% of a hydroxyl-containing vinyl ether represented by the general formula



10 wherein R_2 represents an alkylene group having 1 to 6 carbon atoms.

9. A composition comprising a fluoroolefin copolymer having an inherent viscosity of 0.05 to 2.0 dl/g and composed of

(I) 10 to 70 mole% of monomeric units derived from a fluoroolefin represented by the general formula



20 wherein X is H, Cl F, CF_3 , OCF_3 or OC_3F_7 ,

(II) 5 to 60% of monomeric units derived from a vinyl carboxylate represented by the general formula



30 wherein R_1 represents an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 17 carbon atoms, (III) 5 to 70 mole% of monomeric units derived from a vinyl ether having an alkyl group with 1 to 8 carbon atoms, and

35 (IV) 0 to 30 mole% of monomeric units derived from a hydroxyl-containing vinyl ether represented by the general formula



wherein R_2 represents an alkylene group having 1 to 6 carbon atoms; and an organic solvent.

45 10. The composition of claim 9 wherein the vinyl carboxylate is a vinyl ester of a carboxylic acid having 9 to 10 carbon atoms.

Patentansprüche

50 1. Fluorolefin-Copolymeres mit einer inneren Viskosität von 0,05 bis 2,0 dl/g und bestehend aus (I) 10 bis 70 Mol-% Monomereinheiten, die von einem Fluorolefin der allgemeinen Formel



60 worin X für H, Cl F, CF_3 , OCF_3 oder OC_3F_7 , steht, abgeleitet sind,

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(II) 5 bis 60 Mol-% Monomereinheiten, die von einem Vinylcarboxylat der allgemeinen Formel



worin R₁ für eine aliphatische, aromatische oder alicyclische Kohlenwasserstoffgruppe mit 1 bis 17 Kohlenstoffatomen steht, abgeleitet sind,

(III) 5 bis 70 Mol-% Monomereinheiten, die von einem Vinylether mit einer Alkylgruppe mit 1 bis 8 Kohlenstoffatomen abgeleitet sind,

(IV) 0 bis 30 Mol-% Monomereinheiten, die von einem hydroxylhaltigen Vinylether der allgemeinen Formel



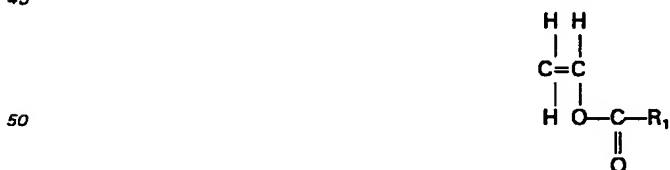
worin R₂ für eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen steht, abgeleitet sind.

2. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß das Fluorolefin Tetrafluorethylen ist.
3. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß das Fluorolefin Chlortrifluorethylen ist.
4. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß das Fluorolefin Hexafluorpropylen ist.
5. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylcarboxylat ein Vinylester einer Carbonsäure mit 9 bis 10 Kohlenstoffatomen ist.
6. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylcarboxylat Vinylbenzoat ist.
7. Copolymeres nach Anspruch 1, dadurch gekennzeichnet, daß es 5 bis 30 Mol.-% der Monomereinheiten (IV) enthält und daß es eine Hydroxylzahl von 20 bis 200 mg KOH/g hat.
8. Verfahren zur Herstellung eines Fluorolefin-Copolymeren, dadurch gekennzeichnet, daß man in Gegenwart eines radiaklischen Initiators und bei einer Temperatur von -20°C bis 130°C 10 bis 70 Mol.-% eines Fluorolefins der allgemeinen Formel



worin X für H, Cl, F, CF₃, OCF₃ oder OC₃F₇ steht,

5 bis 60 Mol-% eines Vinylcarboxylats der allgemeinen Formel



worin R₁ für eine aliphatische, aromatische oder alicyclische Kohlenwasserstoffgruppe mit 1 bis 17 Kohlenstoffatomen steht, 5 bis 70 Mol-% eines Vinylether mit einer Alkylgruppe mit 1 bis 8 Kohlenstoffatomen und 0 bis 30 Mol-% eines hydroxylhaltigen Vinylethers der allgemeinen Formel

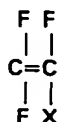


worin R₂ für eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen steht, polymerisiert.

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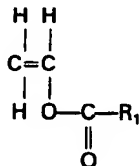
9. Masse, dadurch gekennzeichnet, daß sie ein Fluorolefin-Copolymeres mit einer inneren Viskosität von 0,05 bis 2,0 dl/g und bestehend aus

(I) 10 bis 70 Mol-% Monomereinheiten, die von einem Fluorolefin der allgemeinen Formel



worin X für H, Cl, F, CF₃, OCF₃ oder OC₃F₇, steht, abgeleitet sind,

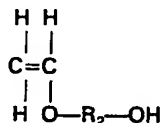
(II) 5 bis 60 Mol-% Monomereinheiten, die von einem Vinylcarboxylat der allgemeinen Formel



worin R₁ für eine aliphatische, aromatische oder alicyclische Kohlenwasserstoffgruppe mit 1 bis 17 Kohlenstoffatomen steht,

(III) 5 bis 70 Mol-% Monomereinheiten, die von einem Vinylether mit einer Alkylgruppe mit 1 bis 8 Kohlenstoffatomen abgeleitet sind,

(IV) 0 bis 30 Mol-% Monomereinheiten, die von einem hydroxylhaltigen Vinylether der allgemeinen Formel



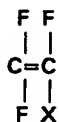
worin R₂ für eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen steht, abgeleitet sind, und ein organisches Lösungsmittel umfaßt.

10. Masse nach Anspruch 9, dadurch gekennzeichnet, daß das Vinylcarboxylat ein Vinylester einer Carbonsäure mit 9 bis 10 Kohlenstoffatomen ist.

Revendications

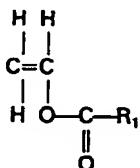
1. Copolymère d'oléfine fluorée ayant une viscosité inhérente de 0,05 à 2,0 dl/g et composé de

(I) 10 à 70 moles % de motifs monomères dérivés d'une oléfine fluorée représentée par la formule générale



dans laquelle X est H, Cl, F, CF₃, OCF₃ ou OC₃F₇,

(II) 5 à 60 moles % de motifs monomères dérivés d'un carboxylate de vinyle représenté par la formule générale

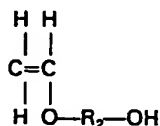


dans laquelle R₁ représente un groupe hydrocarboné aliphatique, aromatique ou alicyclique ayant 1 à 17 atomes de carbone,

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(III) 5 à 70 moles % de motifs monomères dérivés d'un éther de vinyle ayant un groupe alkyle de 1 à 8 atomes de carbone; et

(IV) 0 à 30 moles % de motifs monomères dérivés d'un éther de vinyl hydroxylé représenté par la formule générale



dans laquelle R_2 représente un groupe alkylène ayant 1 à 6 atomes de carbone.

2. Copolymère selon la revendication 1, dans lequel l'oléfine fluorée est le tétrafluoréthylène.

3. Copolymère selon la revendication 1, dans lequel l'oléfine fluorée est le chlorotrifluoréthylène.

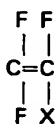
4. Copolymère selon la revendication 1, dans lequel l'oléfine fluorée est l'hexafluoropropylène.

5. Copolymère selon la revendication 1, dans lequel le carboxylate de vinyle est un ester de vinyle d'un acide carboxylique ayant 9 à 10 atomes de carbone.

6. Copolymère selon la revendication 1, dans lequel le carboxylate de vinyle est le benzoate de vinyle.

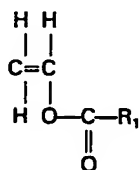
7. Copolymère selon la revendication 1, qui contient 5 à 30 moles % des motifs monomères (IV) et qui a un indice d'hydroxyle de 20 à 200 mg de KOH/g.

8. Procédé de production d'un copolymère d'oléfine fluorée, qui consiste à polymériser, en présence d'un initiateur radicalaire et à une température de -20°C à 130°C , 10 à 70 moles % d'une oléfine fluorée représentée par la formule générale



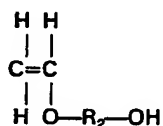
dans laquelle X est H, Cl, F, CF_3 , OCF_3 ou OC_3F_7 ,

5 à 60 moles % d'un carboxylate de vinyle représenté par la formule générale



dans laquelle R_1 représente un groupe hydrocarboné aliphatique, aromatique ou alicyclique ayant 1 à 17 atomes de carbone,

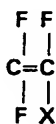
5 à 70 moles % d'un éther de vinyle ayant un groupe alkyle de 1 à 8 atomes de carbone, et 0 à 30 moles % d'un éther de vinyl hydroxylé représenté par la formule générale



dans laquelle R_2 représente un groupe alkylène ayant 1 à 6 atomes de carbone.

9. Composition comprenant un copolymère d'oléfine fluorée ayant une viscosité inhérente de 0,05 à 2,0 dl/g et composé de

(I) 10 à 70 moles % de motifs monomères dérivés d'une oléfine fluorée représentée par la formule générale

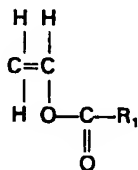


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dans laquelle X est H, Cl, F, CF₃, OCF₃ ou OC₃F₇,

(II) 5 à 60 moles % de motifs monomères dérivés d'un carboxylate de vinyle représenté par la formule générale

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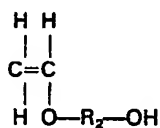
dans laquelle R₁ représente un groupe hydrocarboné aliphatique, aromatique ou alicyclique ayant 1 à 17 atomes de carbone,

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(III) 5 à 70 moles % de motifs monomères dérivés d'un éther de vinyle ayant un groupe alkyle de 1 à 8 atomes de carbone; et

(IV) 0 à 30 moles % de motifs monomères dérivés d'un éther de vinyl hydroylé représenté par la formule générale

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dans laquelle R₂ représente un groupe alkylène ayant 1 à 6 atomes de carbone; et un solvant organique.

10. Composition selon la revendication 9, dans laquelle le carboxylate de vinyle est un ester de vinyle d'un acide carboxylique ayant 9 à 10 atomes de carbone.

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